A Study of Soot and PAH Oxidation in Post-Flame Gases

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The incomplete combustion of gas phase hydrocarbons can lead to toxic emissions from both unwanted fires (Pitts *et al.*, 1994; Zukoski *et al.* 1991) and from industrial processes (You *et al.*, 1994). Typically, both acute toxins such as carbon monoxide (Pitts, 1994) and chronic toxins, such as Polycyclic Aromatic Hydrocarbons (PAH) are simultaneously emitted. Carbon monoxide present in enclosure fires is believed to be responsible for roughly 2/3 of deaths in those situations(Harwood and Hall, 1989). Because of its threat to human health, CO is regulated by the EPA as a criteria pollutant by the Clean Air Act.

PAH are hazardous in their own right; these pollutants exhibit mutagenic and carcinogenic properties (Blakeslee, 1983, Bhatt and Coombs, 1990). In light of the biotoxicity of this class of compounds (see Zaia and Biemann, 1994) , PAH are listed as Hazardous Air Pollutants (HAP) under Title III of the 1990 Clean Air Act Amendments (CAAA). However, PAH may contribute to acute toxicity as well. These molecules are thought to be the key intermediates in the formation of particulate carbon. Both they and the particles that form from them participate in the formation of CO from fires through both the direct oxidation and indirect processes such as radical quenching.

Prediction of heat release rates, opacity of the combustion products, and the amount of CO and other products of incomplete combustion formed in fires have been addressed using hood experiments (see Beyler, 1986; Tewarson and Steciak, 1983; Zukokski *et al.* 1991) and enclosure fires (Grand *et al.* 1986; Morikawa and Yanai, 1986). The composition of the fire emissions in these studies seems to be well correlated with the amount of oxidizer supplied. In many of these studies, the Global Equivalence Ratio, or GER (Cooper, 1994)

has been used to quantify the level of ventilation defined as the moles of carbon divided by the moles of oxygen normalized by the stoichiometric ratio (Pitts, 1994). Therefore GERs greater than one are designated underventilated, GERs less than one are overventilated.

However, in a review by Pitts (1994), results from Morehart (1990) show the equilibrium concentrations of CO increase by a factor of two from 900 - 1500 K for all of the underventilated fires investigated. This suggests that CO formation is a kinetically controlled process. Pitts concludes that the correlation between post-flame temperature and the composition of the gases is not well understood, especially for intermediate temperatures, or where the fires generate copious amounts of smoke.

In our laboratory at GWU a system to study the emissions from overventilated and underventilated diffusion flames has been constructed (Skaggs *et al.* 1996). Both the production of gas phase products(methane, acetylene, carbon monoxide, carbon dioxide, and oxygen) and condensed phase compounds (PAH and soot) from these flames can be followed. The product composition was measured using tunable diode laser absorption spectroscopy, mass spectrometry, laser light extinction, and gas chromatography. The temperature of the effluent stream was varied up to 1300 K using a tube furnace, allowing us to investigate the kinetics of post-flame oxidation.

Some of the key results of our measurements have been:

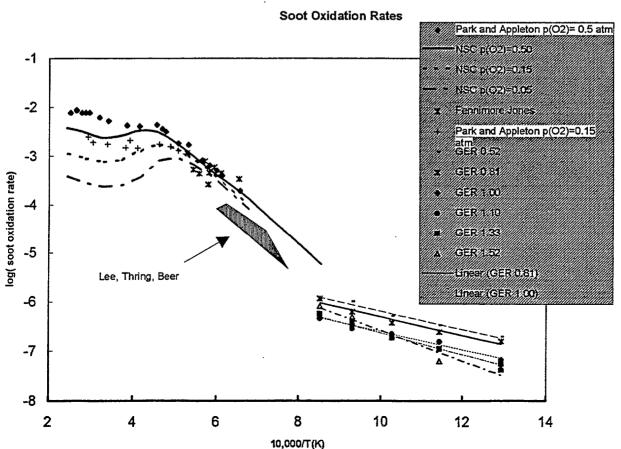- The concentrations of the products of incomplete combustion all increase with increases in GER.

- For lean global stoichiometries, the oxidation chemistry proceeds at a greater rate with increasing tube furnace temperature.
- For rich stoichiometries, evidence exists that chemical processes which include pyrolytic growth and oxidation occur at all furnace temperatures. However, these chemistries undergo a marked change in intensity at temperatures near 900 K.

- The magnitude of the soot oxidation rate agrees qualitatively with what may have been expected from high temperature extrapolations (e.g. Park and Appleton, 1973). However the activation energies for our rates are substantially lower. (Figure 1)

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Figure 1: Comaprison of surface soot oxidation rates from literature values and current measurements. (see Park and Appleton, 1973).

Soot Oxidation Rates